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13. ABSTRACT *(Maximum 200 words)*

The objective of this Phase II Option Small Business Innovation Research project was to design, construct, install, and measure the effectiveness of a full-scale biotrickling filter (BTF) to treat volatile organic compounds (VOCs) and odorous (sulfur) air emissions from wastewater load equalization and treatment tanks at Naval Air Station North Island in San Diego, CA. BTFs are similar to chemical scrubbers, but rely on microorganisms on the packing surface to remove and oxidize contaminants rather than chemicals. The full-scale BTF is 3.1 m (10 ft) in diameter and 9.1 m (30 ft) in height. The reactor is an air downflow system and operates in concurrent fashion with a recirculating water phase. Operation began in early December 1999. System performance has demonstrated good removal of the odorous inorganic compounds (nuisance odors have been substantially reduced) and water-soluble organic hazardous air pollutants, while the less water-soluble VOCs have not been removed completely. Adaptation by the system microorganisms to the low aqueous concentrations of these compounds appears to be occurring slowly, and removal of these compounds is improving as additional biomass growth occurs in the lower media layer. Pressure drops across the entire system are very low and the necessary operator attention is at a minimum.

14. SUBJECT TERMS

Biotrickling filters; Volatile organic compounds; Hazardous air pollutants; Odors; Air treatment

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FINAL REPORT

Grant #: N00014-99-C-0036

PRINCIPAL INVESTIGATOR: A. Paul Togna, Ph.D.

INSTITUTION: Envirogen, Inc.

GRANT TITLE: Development of Biotrickling Filters to Treat Sulfur and VOC Emissions

AWARD PERIOD: 24 November 1998 to 31 May 2000

OBJECTIVE: To design, construct, install, and measure the effectiveness of a full-scale biotrickling filter (BTF) system to treat volatile organic compounds (VOCs) and odorous (sulfur) air emissions from wastewater load equalization and treatment tanks at the Industrial Water Treatment Plant (IWTP) and the Oil Recovery Plant (ORP) at Naval Air Station North Island (NASNI) in San Diego, CA.

The goals of the project were to: (1) evaluate the technical effectiveness of Envirogen's biotrickling filter process on an actual contaminated air stream under real-world conditions, i.e., under fluctuating contaminant loads and discontinuous operating schedules; (2) determine the operating regime of the technology under real-world conditions; (3) obtain data useful for the design of other biotrickling filter systems.

With the above project goals in mind, the sub-objectives of the program were to: (1) obtain removal efficiencies and removal rates (elimination capacities) for both total VOCs and individual contaminants; (2) obtain real-world biotrickling filter operating characteristics, including pressure drop and operator requirements.

APPROACH: A full-scale biotrickling filter was constructed and is being operated at NASNI to treat off-gases generated from four wastewater and oil recovery load equalization and treatment tanks. The primary contaminants of concern for treatment at the industrial wastewater treatment plant are phenol, methylene chloride, methyl ethyl ketone, benzene, toluene, ethylbenzene, xylene (BTEX), and hydrogen sulfide (H_2S). Total VOC and H_2S concentrations range from 7 to 521 ppmv and 1 to 2 ppmv, respectively.

The full-scale biotrickling filter reactor vessel is 3.1 m (10 ft) in diameter and 9.1 m (30 ft) in height (Figure 1). The vessel is constructed entirely of a fiberglass resin polymer. The reactor is an air downflow system and operates in concurrent fashion with a recirculating water phase. Random, inorganic packing is used in two filter beds in series (each 2.1 m in height). The system is automated and controlled through the use of a programmable logic controller that minimizes the need for operator attention. A corrosion-resistant support assembly supports each packing layer. Liquid media containing essential nutrients is recirculated over the packing to maintain a moist biofilm.

Control of the vapor flow rate is accomplished through manual adjustment of valves. The system is operated at a gas empty bed vapor contact time of approximately 36 seconds. Air flow through the system is 2,890 $m^3\ h^{-1}$ [1,700 standard scfm) and the filter bed volume is 31 m^3 (1,100 ft^3). The feed air to the system is supplied under vacuum from the headspace of wastewater Tanks 1A and 1B and oil recovery Tanks 4A and 4B (Figure

2). This air is constantly supplied to the system; however, the supply of contaminants in the air is variable, dependent on the quantity of wastewater being treated through the tanks. Effluent air from the vessel is pulled through a mist eliminator, past a blower, and discharged through two 455 kg (1,000 lb) activated carbon vessels operated in parallel. From the carbon vessels, the air is emitted to the atmosphere.

The liquid recirculation rate is kept manually constant through the use of butterfly valves. The liquid removal rate from the system (60-100 gallons per day) is controlled automatically on a timed cycle by the opening of a liquid discharge valve at the base of the reactor. Make-up water addition to the system occurs automatically when the liquid level in the column drops below a specified level. Concentrated nutrient solutions are added to the system continuously using metering pumps to replace consumed nutrients and nutrients lost during each blowdown cycle. The pH of the recirculating liquid is monitored using an in-line pH probe, and controlled automatically using feedback control to a caustic addition pump providing 20% caustic (by volume).

Figure 1. Photograph of the Full-Scale Biotrickling Filter Reactor (carbon units in foreground).

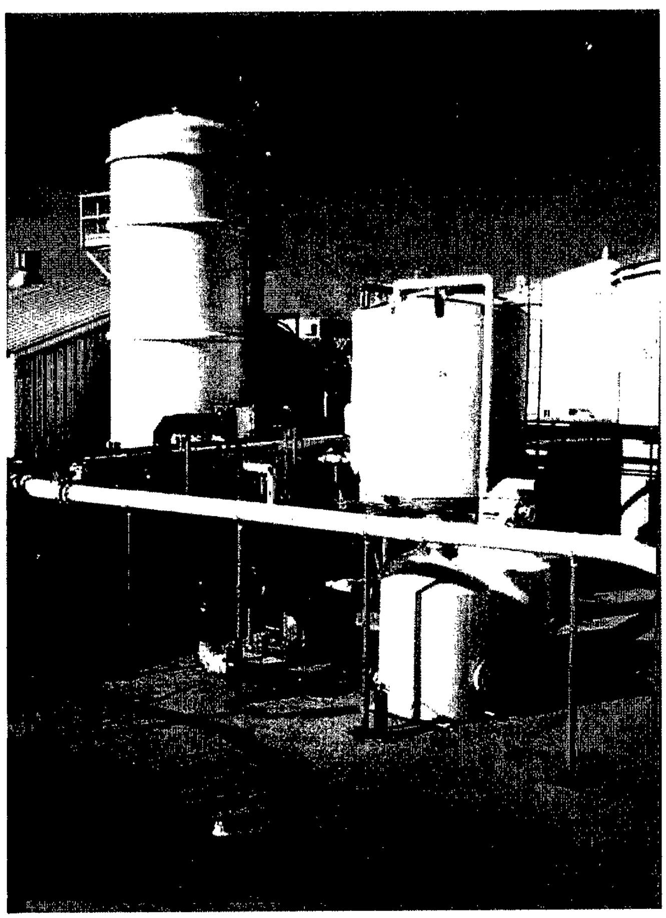
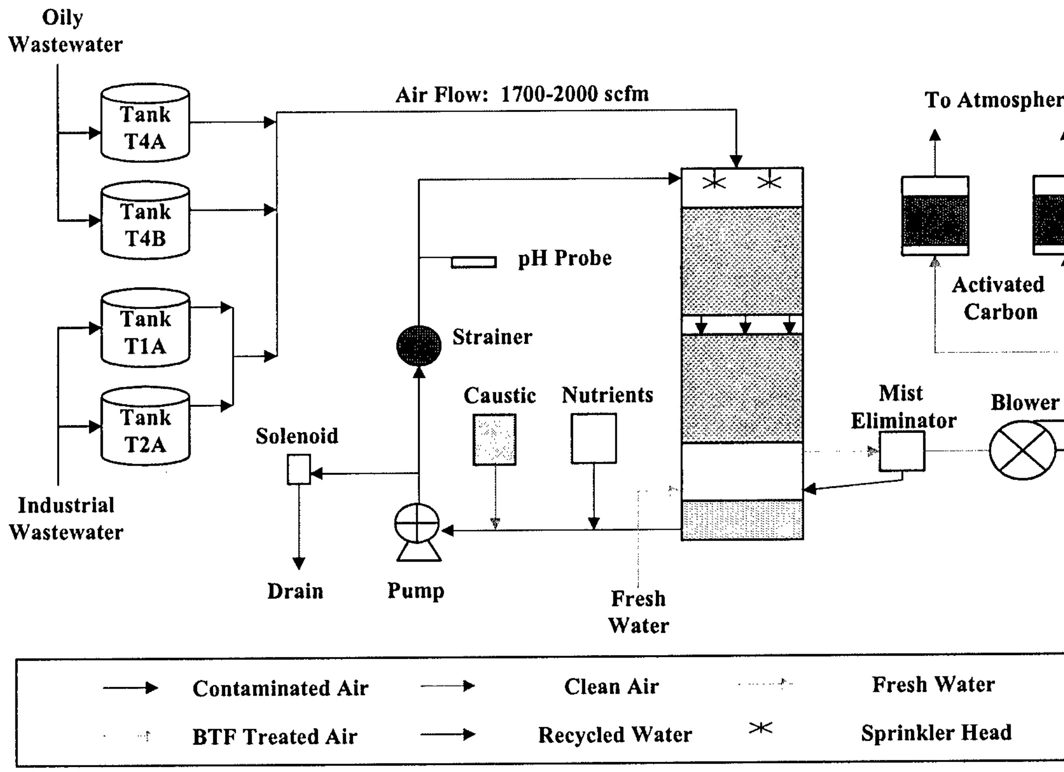


Figure 2. Process Flow of the Biotrickling Filter Reactor.



A computer mounted to the system control panel is used for data logging and remote data acquisition. The status of major system solenoid valves, alarms, and components are logged into a data file whenever a change in status occurs, such as turning the blower on or off. In addition, important operating parameters are monitored and logged into a data file every 10 minutes. These data are periodically accessed and transferred to a computer spreadsheet for analysis.

The system was originally operated without any microbial inoculum to assess the abiotic losses through the system (early December, '99). Once abiotic losses were determined, the system was operated in a batch mode (mid-December 1999). One type of microbial culture was supplied for the project in a dehydrated form. Approximately 11.4 kg (25 lbs) of Formula 20-Bacterial Petrochemical Degraders (Monmouth Bioproducts, Lincroft, NJ) were used to inoculate the system and biofilm development occurred over a one-month period. During this time, 100 lbs of GrowMore® 20-14-11 N/P/K fertilizer (with micronutrients and no carbon) were added to the reactor as an initial nutrient boost. During the batch mode of operation, no liquid was discharged from the reactor. Once system operation began to stabilize (performance increased), the system was operated in a continuous mode (with water discharge and nutrient addition).

On-site air analysis of total organic concentrations was performed using two Eagle™ EM-700 total hydrocarbon analyzers (Irvine, CA) that sampled continuously. Inlet and outlet air was supplied from the reactor to the analyzers through heated sampling lines. The instruments used methane as a calibration gas standard. The data obtained from the analyzers

were automatically logged every 10 minutes into a data acquisition system. Additionally, hydrogen sulfide concentrations were measured on-site using a Jerome Meter® (Jerome, AZ). Inlet and outlet air samples were collected in one liter Tedlar® bags for analysis on-site.

Off-site air analyses of total organic concentrations (EPA Method TO-12) and speciated concentrations (EPA Method TO-14) were conducted by Air Toxics LTD (Folsom, CA). Inlet and outlet air samples were collected in 6-liter SUMMA® canisters and shipped off-site for analysis. For one sampling event, air samples were obtained along the length of the first media bed for analysis by the off-site laboratory.

Water samples for on-site analysis were periodically collected from the biotrickling filter in order to assess the nutritional requirements of the microbes in the reactor. On-site analysis included the use of HACH® (Loveland, CO) measuring kits for the analysis of ammonia-nitrogen, nitrate-nitrogen, phosphate-phosphorus, hardness, and pH. Off-site analysis was performed at the Envirogen's analytical laboratory (Lawrenceville, NJ).

<u>ACCOMPLISHMENTS</u>: The BTF system has been designed, fabricated, and installed. Operation began in early December 1999; since that time, nuisance odors have been substantially reduced.

Hydrogen Sulfide Removal Across the System: Initially, the system was inoculated with a general mixed microbial culture. After adaptation of the microorganisms to the incoming air, hydrogen sulfide inlet concentrations have been consistently reduced by greater than 99% (Figure 3). The formation of daughter product acids from the oxidation of hydrogen sulfide has not inhibited the system performance. These acids have been removed from the media beds via the recirculating liquid phase and neutralized with caustic. The transient loading of the hydrogen sulfide did not affect hydrogen sulfide removal performance.

VOC Removal Across the System: The total VOC removal efficiency for the BTF is currently 50 percent and still improving (Figure 4). Mature biofilms capable of degrading the more water-soluble contaminants rapidly developed at the entrance of the BTF within the first two months of operation, while the media section at the exit of the BTF contained little or no biological growth after six months of operation, and still contains additional capacity for biofilm growth. The more water-soluble contaminants (i.e., aromatics and ketones) are currently being removed with high efficiency (greater than 90 percent), while the less water-soluble contaminants (i.e., aliphatics) are currently being removed with lower efficiency (less than 30 percent). Over the first six months, inlet and outlet samples were collected and speciated removal performance across the BTF steadily increased. Table 1 provides representative data on the removal of individual compounds across the biotrickling filter reactor. The aromatic and ketone removal from this data are representative of consistent system performance. For the less water soluble compounds, performance will improve as the microbes adapt further to the low water concentrations available and continue to grow on these substrates.

Figure 3. Inlet and Outlet Hydrogen Sulfide Concentrations from the Biotrickling Filter Reactor.

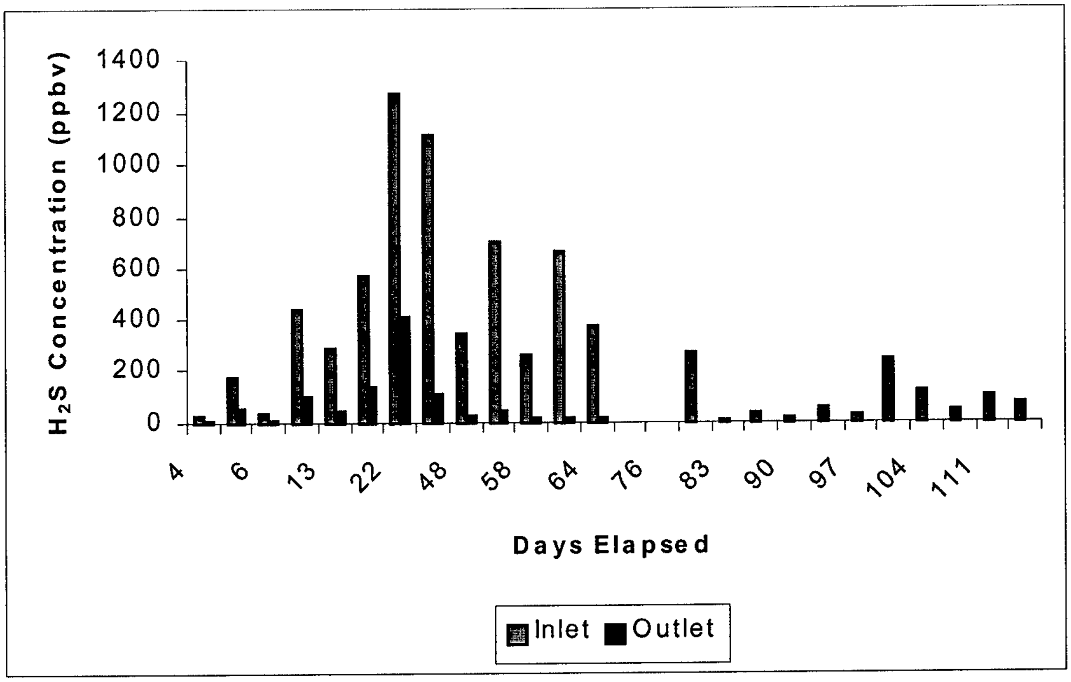


Figure 4. Load, Elimination Capacity, and Removal Efficiency Across the Biotrickling Filter Reactor.

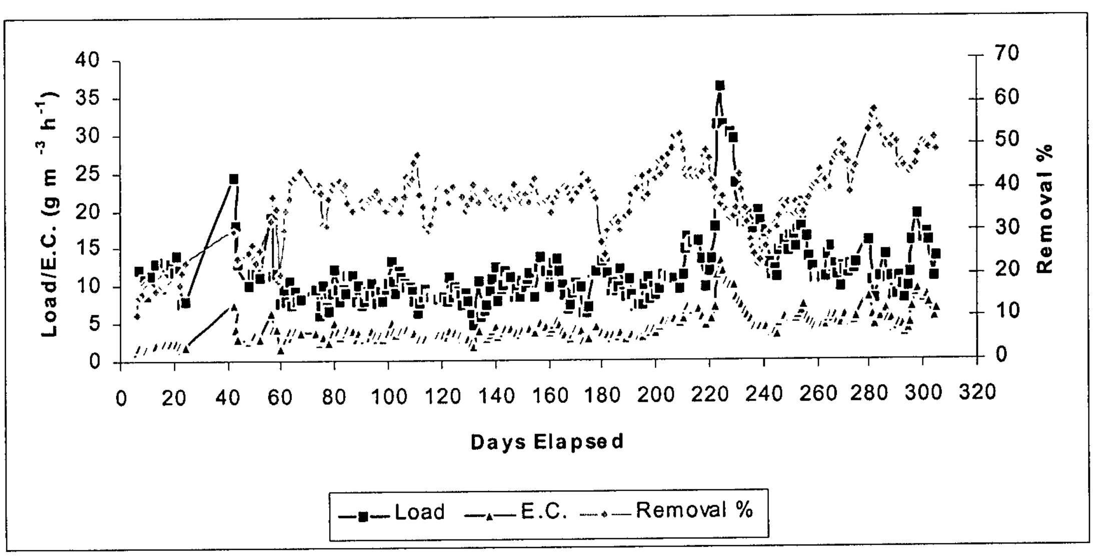


Table 1. Inlet and Outlet Speciated Data for the Biotrickling Filter Reactor (concentrations in ppbv).

6/15/00 TO-14 Data

COMPOUND TYPE/NAME	INLET	OUTLET	Removal %
Aromatics			
Benzene	10	4.1	59.0
Ethanol	200	18	91.0
Ethyl Benzene	130	17	86.9
4-Ethyltoluene	520	59	88.7
m,p-Xylene	560	48	91.4
o-Xylene	250	16	93.6
Toluene	190	29	84.7
1,3,5-Trimethylbenzene	160	26	83.8
1,2,4-Trimethylbenzene	530	26	95.1
Ketones			
Acetone	59	14	76.3
2-Butanone (MEK)	150	4.2	97.2
4-Methyl-2-pentanone	160	4.2	97.4
Aliphatics			
Cyclohexane	33	29	12.1
Cyclohexane, methyl-	230	190	17.4
Heptane	94	54	42.6
Hexane	24	16	33.3
Chlorinated Hydrocarbons			
Chloroform	2.9	2.8	3.4
Methylene Chloride	350	310	11.4
Tetrachloroethene	2.7	2.8	-3.7
Others			
Methyl tert-Butyl Ether	27	11	59.3

Note: Numerous other compounds at small concentrations

VOC Removal Across the First Bed: Samples were collected across the first media bed in series to determine the bed's biodegradation activity. The samples were collected at the inlet to the bed, one and three feet along the bed, and at the outlet of the first media bed. Results for this study are shown in Table 2. Based on the presented data, 40-50% of the aromatics are removed within the first foot of bed material. Little to no removal occurs over the next few feet of bed material, but an additional 10-20% occurs over the last few feet of the bed. The additional removal demonstrated in Table 1 is a result of the degradation activity of the second bed in series. Approximately 80-90% of the ketones are removed in the first foot of bed. The ketone concentrations were shown to be non-detect at the effluent of the first bed, but the detection limit is shown for the purposes of calculating removal efficiencies. The aliphatic and chlorinated compounds showed varying degrees of removal across the first bed (15-75%). The first foot of bed appears to have the most biodegradation activity toward these compounds.

Table 2. TO-14 Speciated Data Along the Length of the First Media Bed (concentrations in ppbv).

10/09/00 TO-14 Data

COMPOUND TYPE/NAME	INLET	1 FT	3 FT	BTWN BEDS	R%-1 FT	R%-3 FT	R%-BTW BED
Aromatics							
Benzene	36	22	25	19	39	31	47
Ethanol	76	18	14	11	76	82	86
Ethyl Benzene	150	77	80	63	49	47	58
4-Ethyltoluene	300	140	140	110	53	53	63
m,p-Xylene	530	240	240	180	55	55	66
o-Xylene	220	120	120	87	45	45	60
Toluene	330	190	200	150	42	39	55
1,3,5-Trimethylbenzene	91	47	53	42	48	42	54
1,2,4-Trimethylbenzene	260	96	86	63	63	67	76
Ketones							
2-Butanone (MEK)	99	18	14	11	82	86	89
4-Methyl-2-pentanone	120	18	14	11	85	88	91
Aliphatics							
Cyclohexane	120	83	110	94	31	8	22
Cyclohexane, methyl-	680	520	670	580	24	1	15
Cyclohexane, ethyl-	1100	350	340	280	68	69	75
Heptane	230	150	140	130	35	39	43
Hexane	67	45	52	45	33	22	33
Chlorinated Hydrocarbons							
Methylene Chloride	150	100	130	120	33	13	20

Operational Parameters: Numerous system operational parameters were measured over the course of the study. Pressure drop across the BTF system, including ducting and media, remained fairly constant at or below 5 inches of water (total). The inlet air and recirculating water temperatures varied with the seasons. The temperature of the incoming air and the recirculating water ranged from 45-95 degrees Fahrenheit and 48-80 degrees Fahrenheit, respectively. During initial start-up, an attempt was made to artificially heat the recirculating water through the use of a heating element. This process was effective for four months until the element became damaged due to biofouling. The use of another element was not attempted as the biomass had developed significantly by this time period. Nutrient and caustic (20% by volume) consumption rates averaged 12.5 lbs and 2.2 gallons weekly. The operator attention required was minimal and averaged less than an hour per week.

Water analyses were conducted on samples of the recirculating water. The pH values were consistently near seven. Nutrient analyses of the collected water samples were initially high. Several formulas were tested until an adequate mix of nitrogen, phosphorus, potassium, and micronutrients was determined. The use of either a nitrate-nitrogen dominant nutrient formulation or an ammonia-nitrogen dominant nutrient formulation provided no improvement in system performance. After adjustments were performed, the suitable nutrient concentrations within the recirculating liquid for ammonia-nitrogen, nitrate-nitrogen, and phosphate-phosphorus were determined to be in the range of 20-200 mg/l, 200-600 mg/l, and 200-600 mg/l, respectively. In addition, it was determined that conductivity measurements should not exceed 10 milliSiemans/cm in the recirculating water.

A system operating manual has been provided to the public works director for the full-scale biotrickling filter reactor. The training of public works personnel on the operation of the system has been completed and the complete transfer of system operation to Navy personnel has been performed.

CONCLUSIONS: The first full-scale biotrickling filter reactor was developed and constructed for the US Navy at Naval Air Station-North Island (San Diego, CA). System performance has demonstrated good removal of the odorous inorganic and organic compounds. The less water soluble compounds have not been removed completely. Adaptation by the system microorganisms to the low aqueous concentrations of these compounds appears to be occurring slowly, and performance is improving as additional biofilm growth occurs in the lower media layer. Pressure drops across the entire system are very low and the necessary operator attention is at a minimum. An adequate nutrient supply has been experimentally determined and is now supplied to the system for sufficient microbial growth. As a large fraction of the biodegradation activity has been shown to occur in the first media bed, additional bed volume exists for larger loads of soluble compounds to be introduced to the system without a decline in performance. The US Navy currently has received transfer of the system and is operating the reactor successfully.

SINGNIFICANCE: The full-scale BTF system is the first of its kind developed for the US Navy. Biological air treatment technologies have not been used in the U.S. to the same extent as in Europe, primarily due to cheaper supplemental fuel costs in the US and a lack of full-scale experience. However, biotreatment processes are environmentally friendly, less costly to operate, and produce only non-hazardous by-products and minimum levels of carbon dioxide. No carbon monoxide, nitrogen oxides, or sulfur oxides are produced. The successful implementation of the first large-scale BTF process in the US for VOC treatment may provide the stimulus for the general use of biotreatment processes for air pollution control in the US.

PATENT INFORMATION: None

AWARD INFORMATION: None

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1. Frazer, L. April 2000. "The trickle-down theory of cleaner air," Environmental Health Perspectives, 108(4), pp. A178- A180.

2. Webster, T.S., A.P. Togna, W.J. Guarini, B. Hooker, and H. Tran. "Operation of a Full-Scale Biotrickling Filter Reactor to Treat Off-Gas Emissions Generated from an Industrial Wastewater Treatment Plant," Proceedings of the Water Environment Federation Specialty Conference Entitled Odors and VOC Emissions 2000, Cincinnati, Ohio, April 16-19, 2000.

3. Webster, T.S., A.P. Togna, W.J. Guarini, B. Hooker, H. Tran, J. Sanfedele, J. Olson. "Treatment of Vapor Emissions Generated from an Industrial Wastewater Treatment Plant Using a Full-Scale Biotrickling Filter Reactor," Proceedings of the 93rd Annual Air & Waste Management Association Conference and Exhibition, Salt Lake City, Utah, June 18-22, 2000. Paper # 00-353.